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CLAIMS

[Claim(s)]

[Claim 1] A manufacture method of a settling silica granulation object which average grain size is 60 micrometers or more, and is characterized by for average grain size carrying out 5-30 section mixing, and corning settling silica powder 20 micrometers or less to the settling silica powder 100 with a particle degrees of hardness [10-30g] section.

[Claim 2] A manufacture method according to claim 1 of corning said two sorts of settling silica powder with a roll type granulating machine.

[Claim 3] A bulking agent for elastomer reinforcement characterized by consisting of a settling silica granulation object acquired by manufacture method according to claim 1 or 2.

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the bulking agent for elastomer reinforcement which consists of the manufacture method of the granulation object by mixing of two or more sorts of settling silicas, and a granulation object acquired by this manufacture method.

[0002]

[Description of the Prior Art] A settling silica is called common-name white carbon, the simple grain children of silica impalpable powder usually gather lightly, and have become an about 1-5-micrometer condensation grain, and belongs to the lightest category also in fine particles, and tends [very] to become dust. So, the way silica impalpable powder prepares a ventilator, a dust-proofing device, etc. when fear of silicosis deals with this powder in the rubber industry which carries out the combination activity of this since it is hardly desirable to inhale dust although it is known that there is nothing for reasons of sanitation is taken. However, a little [the], inhalation was not escaped, but the working condition was spoiled, loss of this impalpable powder was also unescapable, a fluidity is bad, the fine particles had many handling top difficulties, such as blowdown supply from a hopper, and transport, and a fluid improvement was desired again. furthermore, the fine particles of a settling silica -- ** -- a package and freight increased highly and non-economy was also caused.

[0003] If the reinforcement engine performance which is the original function is considered to a subject when such pulverized coal is originally used as an elastomer reinforcing filler, of course, it is desirable that it is pulverized coal with sufficient dispersibility. However, as mentioned above, from various difficulties, the granular article silica which dispersibility and the reinforcement engine performance have was demanded, and the various granulation methods have been considered. For example, the method of obtaining a granular article is indicated by carrying out spray drying of the high concentration precipitate silicic-acid slurry to JP,56-41566,B and JP,2-302312,A. However, this method of an improvement of the workability whose particle diameter is the granulation article original object that relative bulk density is also low small again, or storage and the improvement of an transportation cost is insufficient.

[0004] Moreover, it is well-known to manufacture precipitate silica granulatio with dry process by carrying out the precompression of the powdered precipitate silica to a reduced pressure list first with a revolution roller under the activity of mechanical pressure, and pressing precipitate silica granulatio by the mold groove attached in at least one roller (based on the West Germany country patent specification No. 1807714 publication). However, although the precipitate silica granulatio which is dry process in this way, and was manufactured without the additive is excellent in the point which does not contain actually good dispersibility and coarse grain, fines are intermingled and it causes dust generating. Moreover, fines generate fines by wear according to handling also as ****** according to screen immediately after a compression-molding process and a crushing process highly [the haulage stability and storage stability of this granulatio]. This causes [of dust] scattering, in case a user deals with granulatio. Moreover, if there are

many fines, the silica interlocking nature at the time of compound raw material kneading **** will produce the problem that mixing time starts for a long time bad. Moreover, although the defect which is a granulation object of being easy to powder can improve to be sure if a compression pressure is made high, the dispersibility to rubber gets bad to a polar body.

[0005] Then, since closed types, such as a Banbury mixer, became [the kneading machine] in use in recent years, the interlocking nature not only at reduction of transport cost but the time of a compound raw material kneading lump was good, and a precipitate silica granulation object to which the function as an elastomer reinforcing filler moreover does not fall was desired. The object of this invention has dispersibility required as an elastomer reinforcing filler, and good reinforcement nature, and they are to have the particle diameter more than fixed, and offer a precipitate silica granulation object with high particle reinforcement, and its manufacture method. It is the object of this invention to offer the precipitate silica granulation object which is more specifically in the range whose mean particle diameter is 0.5-5mm, and has preferably 10-30g of particle reinforcement in the range of 15-25g. Furthermore, this invention is to offer the bulking agent for elastomer reinforcement which has the physical properties which were excellent as mentioned above.

[0006]
[Means for Solving the Problem] It came to complete a header and this invention for improvement of workability, storage, and transport of a granulation object acquired by mixing two sorts of a settling silica for example, with a roll type granulating machine as a result of this invention persons' repeating research improving extremely, without acquiring rubber physical properties equivalent to an impalpable powder silica as an elastomer reinforcing filler, and spoiling dispersibility.

[0007] That is, this invention relates to a manufacture method of a settling silica granulation object which is 60 micrometers or more in average grain size, and is characterized by carrying out 5-30 section mixing and coming settling silica powder with an average grain size of 20 micrometers or less to the settling silica powder 100 with a particle degrees of hardness [10-30g] section. Furthermore, this invention relates to a bulking agent for elastomer reinforcement characterized by consisting of a settling silica granulation object acquired by above-mentioned manufacture method. Hereafter, this invention is explained to details.

[0008] A settling silica used for a manufacture method of this invention as a raw material can use a well-known settling silica as it is. Such a settling silica can be manufactured by well-known

method. For example, when a sodium silicate aqueous solution and a sulfuric acid are used, according to a neutralization reaction type shown below, a silica slurry is obtained, and when required subsequently to filtration, rinsing, and a desiccation pan, moderate grinding is performed and it is manufactured.

Na2 O-nSiO2+H2SO4+H2O -> nSiO2 and H2O **+Na2SO4

[0009] It is 60 micrometers or more in average grain size manufactured by above-mentioned process, and with a particle degrees of hardness [10-30g] settling silica powder is used as an elastomer reinforcing filler until now. It is not desirable from effectiveness of an activity and productivity worsening [average grain size] by less than 60 micrometers, since relative bulk density as a original object is low, and relative bulk density as a granulation article not improving. In addition, although there is especially no maximum of average grain size, it is about 1mm practical and is usually about 200 micrometers. Moreover, it is at best still more desirable that it is the range of 10-30g, and a particle degree of hardness has 15-good 25g. This range is crossed, when too hard, a particle of the granulation object of this invention method itself becomes hard, and distribution in rubber worsens. Moreover, when too soft, the amount of fines increases that a particle is soft even if it mixes two sorts, as a result destruction of a particle tends to break out. In addition, a particle degree of hardness is the value measured according to a method of JISK-6221 mentioned later.

[0010] A roll application-of-pressure granulation article which was 60 micrometers or more in mean particle diameter, and adjusted that which carried out crushing of the desiccation floc and carried out the particle size regulation, for example, a granulatio article which carried out spray drying, roll pressure, and a mill opening, and was manufactured as with a particle degrees of hardness [10-30g] precipitate silica powder can use it suitably.

[0011] By the manufacture method of this invention, it is 60 micrometers or more in average grain size, and a granulation object is manufactured to the settling silica powder 100 with a particle degrees of hardness [10-30g] section by mixing settling silica powder with an average grain size of 20 micrometers or less, and coming the five to 30 section. Since a settling silica with an average grain size of 20 micrometers or less cannot do a thing of relative bulk density which in two-sort mixing cannot fully fill a silica comrade's opening but can be satisfied as a granulation article if average grain size of 20 micrometers is exceeded, it is not desirable. Moreover, although there is especially no limit in a minimum of average grain size of a settling silica with an average grain size of 20 micrometers or less, from a practical viewpoint, it is about

5 micrometers. In a field and the elastomer field as which comparatively smooth surface states, such as agricultural chemicals, special paper, and an elastomer (hypoviscosity article), are required, silica powder currently used for a hypoviscosity type which thinks dispersibility as important can be used for a settling silica with an average grain size of 20 micrometers or less. Moreover, a silica of a big average grain size may be ground.

[0012] moreover, a mixing ratio of settling silica powder with an average grain size of 20 micrometers or less -- since an opening between silicas is not fully filled and relative bulk density does not improve although product yield and productivity improve when a rate is the less than 5 sections, interlocking nature to an elastomer used as a policy objective and dispersibility worsen, as a result reinforcement engine performance is worsened. On the other hand, if it exceeds the 30 sections, product yield and productivity will worsen and an improvement also of transport made into the object and improvement in productivity will be impossible. When manufacturing a granulation object by mixing and coming settling silica powder with an average grain size of 20 micrometers or less in the range of the five to 30 section to it, even if it becomes high, transport and improvement in productivity are also improve and relative bulk density make into the object of a granulation article blends with an elastomer, interlocking nature, dispersibility, and reinforcement engine performance can acquire a good granulation object. A mixed rate of settling silica powder with an average grain size of 20 micrometers or less is the range of the ten to 25 section preferably.

[0013] By manufacture method of this invention, it mixes at a predetermined rate and, subsequently the two above-mentioned sorts of settling silica powder is corned. The above-mentioned mixing can be performed with a conventional method. Moreover, if a granulation method is dry process, it will be acquired, and there is no limit. A granulation method is roughly divided and has three sorts, mixing granulation, a compulsive granulation, and a heat utilization granulation. It is desirable to use a compulsive granulation method especially in this invention. There is the knockout granulation method for using compression forming, screws, etc., such as a compression roll, a briquetting roll, and a making tablet, etc. among the compulsive granulation methods. It is desirable to use compression forming in this invention.

[0014] Compression forming using a compression roll is explained below. A compacting machine using a compression roll is marketed as a roll type granulating machine. The operating conditions at the time of using two roll type (path 160mmphi, width of face of 60mm) making machines with a power of 3.7kW as a roll type granulating machine are as follows. In addition, it is in a roll a slot, with [smoothness,] a wave, etc. First, a fine-particles raw material paid to an

up hopper is pushed in between press rollers, being pressurized by revolution of a feed screw (0.75W). Along with a roll revolution (15RPM), it is compressed, a particle becomes dense and **** rare ****** is formed in tabular. A reduction rate of a gap of a lower roll determines moulding pressure from an interlocking point, and specific gravity and reinforcement of a Plastic solid are determined. An oil hydraulic cylinder adjusts a prcssure to the target pressure.

[0015] By carrying out mixing granulation of two sorts of settling silicas by this invention method, dispersibility is good and, moreover, a good silica granulation object of processability, productivity, and rubber reinforcement nature is acquired. A settling silica used for a silica granulation object and its manufacture method of this invention method has desirably a good thing whose BET specific surface areas are 150-250m2 / g and whose oil absorption is 150-250ml / 100g. Especially a well-known method is not restricted but a method of filling up an elastomer with a granulation object of this invention method can be adopted. For example, in kneading to organic solid rubber, such as SBR, it can carry out using a roll or a Banbury mixer.

[0016]

[Example] Hereafter, the example of this invention is explained. In addition, measurement of the object sex test of the particle degree of hardness of each example, dispersibility, processability, and an elastomer constituent and the object sex test (Mooney viscosity trial) of non-vulcanizate was performed by the method shown below.

1) JIS of a particle degree-of-hardness measuring method carbon black particle degree-of-hardness measuring method It measured according to the hardness measuring method of K6221 and a 6.3.3 granulation particle.

2) Relative-bulk-density fixed weight was slushed into the measuring cylinder, and it considered as the numeric value which read the numeric value at that time and was broken by weight.

[0017]

3) O and an ordinary thing were displayed by ** and the bad thing was displayed for what has the high productivity at the time of a productivity granulation by x.

4) About a visual judgment and vulcanizate nature of a dispersibility vulcanized-rubber piece, the outstanding thing was displayed by O, and the ordinary thing was displayed by O.

5) The workability at the time of a roll kneading activity and mixing nature were excellent, and

O and a middle thing were displayed by ** and they displayed the bad thing for the outstanding thing by x, so that there were many amounts which processability relative bulk density can teach highly to one batch.

6) Vulcanizate property (tensile strength) JIS It measured according to the method of examining K6301.

7) It measured with the L type rotor at the temperature of 125 degrees C using the Mooney viscosity Mooney viscometer (the Shimadzu make, SMV-200 mold viscometer).

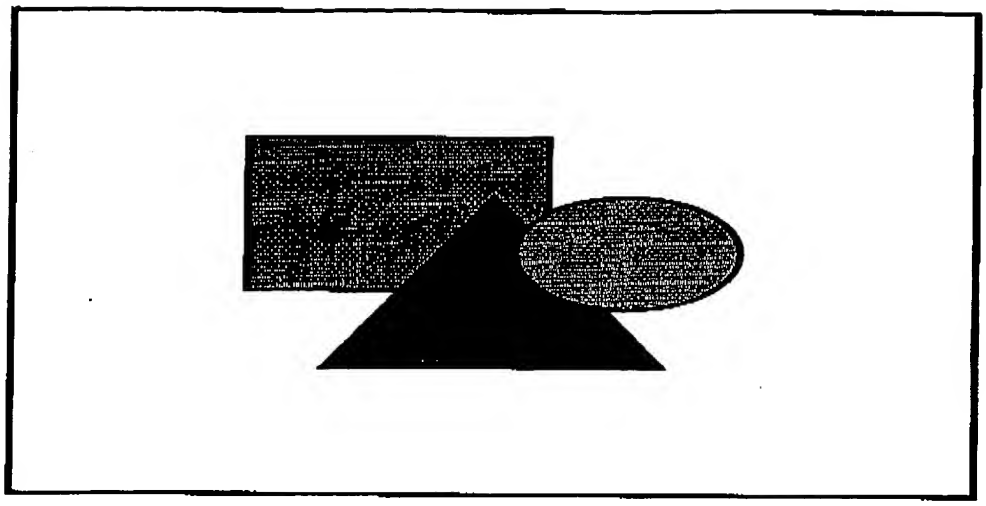
[0018] As opposed to examples 1-3 and example of comparison 1 average grain-size 185 micrometerm, 250g [/l.] relative bulk density, 200m 2 of BET specific surface areas / g, the particle degree of hardness of 19g, the oil absorption of 200ml / precipitate silica (trade name; nip seal AQ (Nipsil)) 100 100g section the nip seal AQ -- grinding -- average grain-size about 18micrometerm, the precipitate silicas (precipitate silica A) 5, 20, and 30 of 125g/l. of relative bulk density, or the 40 sections -- a roll pressure type granulating machine (turbo industrial company make --) The test machine WP 230-80 is used. The roll gap of 2.1mm, the compression pressure of 0.5t/cm, And mixing granulation was carried out by roll rotational frequency 15.6rpm, grain size was further adjusted to the range of 1mm - 5mm, and the with the relative bulk density 276 shown in a table 1 - 300 g/l, and a particle degrees of hardness [19-22g] precipitate silica granulation object was acquired. In addition, feed of fine particles was carried out by 160rpm using the screw feeder of 60mmphi. The fine-particles speed of supply at this time was about 130 to 150 kg/hr.

[0019] Subsequently, it is the granulation object 50 section obtained above, the styrene butadiene copolymer rubber (SBR1502; Japan Synthetic Rubber Co., Ltd. make) 100 section, and a vulcanizing agent. as the sulfur 2.0 section, the D(diphenylguanidine) 1.2 section of marketing as a vulcanization accelerator, the DM(dibenzothiazyl disulfide) 0.8 section, and a vulcanization assistant -- the zinc oxide 3 section and stearin acid -- the 1 section, the PEG(polyethylene glycol) #4000(product made from first heavy chemicals) 2 section was scoured further, using a 8 inch roll as an activator, it kneaded at the temperature of 30 degrees C, and the rubber constituent was obtained (examples 1-3, example 1 of a comparison). Various object sex test was performed about the thing and vulcanizate (what was vulcanized for 10 minutes at 150 degrees C) which are not vulcanized about the rubber constituent of the four above-mentioned points, and the result was shown in a table 2 together with the processability assessment at the time of roll kneading.

[0020] As opposed to example 4 - 6 average grain-size 85micrometerm, 220g [/l.] relative bulk density, BET specific surface area190m2/g, the particle degree of hardness of 16g, the oil absorption of 210ml / precipitate silica (trade name; nip seal (Nipsil) AQ-S) 100 100g section Nip seal AQ-S was ground, mixing granulation of the average grain size of about 18 micrometers, the precipitate silicas (precipitate silica B) 5 and 20 of 127g/l. of relative bulk density, or the 30 sections was carried out like examples 1-3 using the roll pressure type granulating machine, grain size was further adjusted to the range of 1mm - 5mm, and the with the relative bulk density 285 shown in a table 1 - 290 g/l, and a particle degrees of hardness [20-21g] precipitate silica granulation object was acquired. The acquired granulation object was kneaded by the same presentation as examples 1-3, and the rubber constituent was obtained (examples 4-6). Various object sex test was performed about the thing and vulcanizate (what was vulcanized for 10 minutes at 150 degrees C) which are not vulcanized about these rubber constituents, and the result was shown in a table 2 together with the processability assessment at the time of roll kneading.

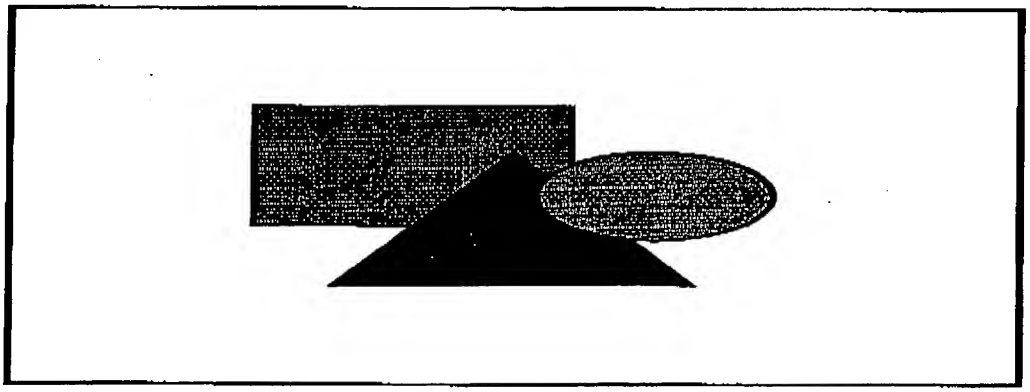
[0021] The nip seal AQ was independently adjusted on the same conditions as examples 1-3 among the precipitate silicas used for two-sort mixing granulation in the two to example of comparison 4 examples 1-3, and the roll pressure type granulating machine adjusted grain size after the granulation (example 2 of a comparison). The precipitate silica A was independently adjusted on the same conditions as examples 1-3 among the precipitate silicas used for two-sort mixing granulation in the examples 1-3, and the roll pressure type granulating machine adjusted grain size after the granulation (example 3 of a comparison). The nip seal AQ was pulverized, it considered as mean-particle-diameter 10micrometerm and the impalpable powder of 80g/l. of relative bulk density, and that which does not corn was obtained as a precipitate silica C (example 4 of a comparison). Using these silicas, the rubber constituent was obtained like examples 1-3, various object sex test was performed about the thing and vulcanizate (what was vulcanized for 10 minutes at 150 degrees C) which are not vulcanized about each rubber constituent, and the result was shown in a table 2 together with the processability assessment at the time of roll kneading.

[0022]



[0023]

[A table 2]



[0024] As for the granulation article of this example, dispersibility, processability, and tensile strength showed the value almost equivalent to the precipitate silica C of the example 4 of a comparison so that clearly from tables 1 and 2. This shows that distributed combination is carried out to homogeneity in a rubber constituent, although, as for the granulation silica of this invention, relative bulk density became large. Moreover, about the productivity at the time of obtaining a granulation article, it turns out that the yield of one pass in a granulating machine is also further excellent, and the productivity in a total is also excellent, without the relative bulk density of the precipitate silica in front of a granulation becoming extremely small.

[0025]

[Effect of the Invention] According to this invention, it is good, and it has the particle diameter more than fixed, and dispersibility required as an elastomer reinforcing filler and reinforcement nature can offer a precipitate silica granulation object with high particle reinforcement, and its manufacture method. Furthermore, according to this invention, the bulking agent for elastomer reinforcement which has the physical properties which were excellent as mentioned above can be obtained.

TECHNICAL FIELD

[Industrial Application] This invention relates to the bulking agent for elastomer reinforcement which consists of the manufacture method of the granulation object by mixing of two or more sorts of settling silicas, and a granulation object acquired by this manufacture method.

EFFEKT OF INVENTION

[Effect of the Invention] According to this invention, it is good, and it has the particle diameter more than fixed, and dispersibility required as an elastomer reinforcing filler and reinforcement nature can offer a precipitate silica granulation object with high particle reinforcement, and its manufacture method. Furthermore, according to this invention, the bulking agent for elastomer reinforcement which has the physical properties which were excellent as mentioned above can be obtained.

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(54)【発明の名称】　沈殿法シリカ造粒体の製造方法及びエラストマー補強用充填剤

(57)【要約】
【目的】　エラストマー補強充填剤として必要な分散性及び解砕性が良好であり、一定以上の粒子径を有し、かつ粒子強度が高い沈殿シリカ造粒体、及びその製造方法、並びにエラストマー補強用充填剤の提供。
【構成】　平均粒度が60μm以上で、且つ粒子硬度10～30gの沈殿法シリカ粉末100部に対して、平均粒度が20μm以下の沈殿法シリカ粉末を5～30部混合し、造粒する沈殿法シリカ造粒体の製造方法。この製造方法により得られた沈殿法シリカ造粒体からなるエラストマー補強用充填剤。

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【特許請求の範囲】

【請求項1】　平均粒度が60μm以上で、且つ粒子硬度10～30gの沈殿法シリカ粉末100部に対して、平均粒度が20μm以下の沈殿法シリカ粉末を5～30部混合し、造粒することを特徴とする沈殿法シリカ造粒体の製造方法。

【請求項2】　前記2種の沈殿法シリカ粉末をロール式造粒機で造粒する請求項1記載の製造方法。

【請求項3】　請求項1又は2記載の製造方法により得られた沈殿法シリカ造粒体からなることを特徴とするエラストマー補強用充填剤。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は、沈殿法シリカ2種以上の混合による造粒体の製造方法、及びこの製造方法により得られた造粒体からなるエラストマー補強用充填剤に関する。

【0002】

【従来の技術及び発明が解決しようとする課題】沈殿法シリカは通称ホワイトカーボンといわれ、シリカ微粉末の単粒子は通常軽く結合して1～5μm程度の凝集粒になっており、粉体の中でも最も軽い部類に属し、非常にダストになりやすい。それ故、シリカ微粉末はケイ肺のおそれはほとんどないことが知られているとはいえ、粉塵を吸入することは衛生上好ましくないので、これを配合使用するゴム工業などにおいては、該粉末を取り扱う場合、換気装置、防塵装置等を設ける方法が取られている。しかしながら、その若干は吸入を免れず作業条件を損ない、該微粉末の損失も不可避的でありました。その粉体は流動性が悪くホッパーからの排出供給、輸送等取扱上難点が多く、流動性の改善が望まれていた。更に、沈殿法シリカの粉体は、嵩高く包装、運搬費が嵩み不経済も招いていた。

【0003】元来、このような微粉体をエラストマー補強充填剤として用いた場合、その本来の機能である補強性能を主体に考えるならば、分散性の良い微粉体であることが望ましいのは勿論である。しかしながら、上述のように種々の観点から、分散性、補強性能とも問題ない粒状品シリカが要望されて、種々の造粒方法が検討されてきた。例えば、特公昭56－41586号、特開平2－302312号には高濃度沈殿ケイ酸スラリーを噴霧乾燥することにより粒状品を得る方法が開示されている。しかし、この方法では粒子径が小さく又、嵩比重も低く造粒品本来の目的である作業性の改善や貯蔵及び輸送費の改善が不十分である。

【0004】又、粉末状沈殿シリカを減圧並びに機械的圧力の使用下に回転ローラーで初めに予備圧縮し、少なくとも一つのローラーに取り付けられた型枠によって沈殿シリカ顆粒を圧縮成形することにより、沈殿シリカ顆粒を乾式法で製造することは公知である（西ドイツ国特許明細書第1807714号記載による）。しかし、こうして乾式法で且つ添加剤なしで製造した沈殿シリカ顆粒は実際良好な分散性及び強粒を含まない点では優れているが、微粉が残存し、粉塵発生の原因となる。また、該顆粒の運搬安定性及び貯蔵安定性も高くなく、圧縮成形工程及び粉砕工程の直後に微粉を篩別けしたとしても、ハンドリングによる摩耗によって微粉が生成する。これはユーザーが顆粒を取り扱う際にダストの飛散の原因となる。又、微粉が多いとコンパウンド原料練りこみ時のシリカ食い込み性が悪く練り時間が長く掛かるという問題を生じる。また、圧縮圧を高くすれば、造粒体の粉化し易いという欠点は確かに改善できるが、ゴムへの分散性が極端に悪くなる。

【0005】そこで、近年混練機がバンバリーミキサー等の密閉式が主流になったこともあって、輸送コストの低減のみならずコンパウンド原料練り込み時の食い込み性が良く、しかもエラストマー補強充填剤としての機能が落ちない沈殿シリカ造粒体が望まれていた。本発明の目的は、エラストマー補強充填剤として必要な分散性及び補強性が良好であり、一定以上の粒子径を有し、かつ粒子強度が高い沈殿シリカ造粒体、及びその製造方法を提供することにある。より具体的には、例えば、平均粒子径が0.5～5mmの範囲にあり、粒子強度が10～30g、好ましくは15～25gの範囲にある沈殿シリカ造粒体を提供することが、本発明の目的である。さらに本発明は、上記のように優れた物性を有するエラストマー補強用充填剤を提供することにある。

【0006】

【課題を解決するための手段】本発明者らは研究を積み重ねた結果、沈殿法シリカの2種を、例えばロール式造粒機で混合することにより得られた造粒体は、エラストマー補強充填剤として微粉末シリカと同等のゴム物性が得られ、且つ分散性を損ねることなく、作業性、貯蔵、輸送の改善が極めて向上することを見出し、本発明を完成するに至った。

【0007】即ち、本発明は、平均粒度60μm以上で、且つ粒子硬度10～30gの沈殿法シリカ粉末100部に対して平均粒度20μm以下の沈殿法シリカ粉末を5～30部混合し、造粒することを特徴とする沈殿法シリカ造粒体の製造方法に関する。さらに本発明は、上記製造方法により得られた沈殿法シリカ造粒体からなることを特徴とするエラストマー補強用充填剤に関する。以下、本発明を詳細に説明する。

【0008】本発明の製造方法に原料として用いる沈殿法シリカは公知の沈殿法シリカをそのまま用いることができる。そのような沈殿法シリカは、公知の方法で製造できる。例えば、ケイ酸ソーダ水溶液と硫酸を用いた場合、以下に示す中和反応式に従って、シリカスラリーを得て、ついで濾過、水洗及び乾燥さらに必要な場合には適度の粉砕を行い製造される。

$Na_2O \cdot nSiO_2 + H_2SO_4 + H_2O \rightarrow nSiO_2 \cdot H_2O \downarrow + Na_2SO_4$

【0009】上述の製法で製造された平均粒度60μm以上で、且つ粒子硬度10～30gの沈殿法シリカ粉末はこれまでもエラストマー補強充填剤として使用されている。平均粒度が60μm未満では、原体としての嵩比重が低いため作業及び生産性の効率が良くなり、造粒品としての嵩比重が向上しないことから好ましくない。尚、平均粒度の上限は特にないが、実用的には1mm程度であり、通常は200μm程度である。また、粒子硬度は10～30gの範囲であることが良く、さらに好ましくは15～25gが良い。この範囲を超え、硬すぎた場合、本発明法の造粒体自体の粒子が硬くなり、ゴム中での分散が悪くなる。又、軟らかすぎた場合、2種を混合しても粒子が軟らかく、ひいては粒子の破壊が起きやすく微粉量が多くなる。尚、粒子硬度は後述するJIS K－6221の方法に従って測定した値である。

【0010】平均粒径60μm以上で、且つ粒子硬度10～30gの沈殿シリカ粉末としては、例えば、乾燥塊状体を粗砕し整粒したもの、噴霧乾燥した球粒品、ロール圧、ロール間隙を調整し製造されたロール加圧造粒品などが好適に使用できる。

【0011】本発明の製造方法では、平均粒度60μm以上で、且つ粒子硬度10～30gの沈殿法シリカ粉末100部に対して、平均粒度20μm以下の沈殿法シリカ粉末を5～30部を混合し、造粒することで造粒体を製造する。平均粒度20μm以下の沈殿法シリカは、平均粒度20μmを超えると2種混合の場合、シリカ同志の空隙を十分に埋めることができず、造粒品として満足できる嵩比重のものができないので好ましくない。また、平均粒度20μm以下の沈殿法シリカの平均粒度の下限には特に制限はないが、実用的な観点からは、5μm程度である。平均粒度20μm以下の沈殿法シリカは、歯薬、特殊紙、エラストマー（低粘度品）等、比較的緩やかな表面状態が要求される分野、エラストマー分野においては、分散性を重視する低粘度タイプに使用されているシリカ粉末が使用できる。又、大きな平均粒度のシリカを粉砕したものであっても良い。

【0012】また、平均粒度20μm以下の沈殿法シリカ粉末の混合比率が5部未満の場合、製品収率や生産性は向上するが、シリカ同士間の空隙が十分に埋められず、嵩比重が向上しないので、最終目標となるエラストマーへの食い込み性、分散性が悪くなり、ひいては補強性能を悪化させる。一方30部を超えると、製品収率や生産性が悪くなり、目的とする輸送、生産性の向上も改善ができない。それに対して、平均粒度20μm以下の沈殿法シリカ粉末を5～30部の範囲で混合し造粒することにより造粒体を製造する場合は、造粒品の目的とする嵩比重が高くなり、輸送、生産性の向上も改善され、エラストマーに配合しても良い込み性、分散性、補強性

能とも良好な造粒体を得ることができる。平均粒度20μm以下の沈殿法シリカ粉末の混合割合は、好ましくは10～25部の範囲である。

【0013】本発明の製造方法では、上記2種の沈殿法シリカ粉末を所定の割合で混合し、次いで造粒する。上記混合は、乾法により行うことができる。また、造粒方法は乾式法であれば特に限定はない。造粒方法は、大きく分けて混合造粒、強制造粒及び熔融造粒の3種がある。本発明では特に強制造粒法を用いることが好ましい。強制造粒法には、圧縮ロール、ブリケッティングロール、打錠等の圧縮成形法やスクリュー等を用いる押し出し造粒法等がある。本発明では、圧縮成形法を用いることが好ましい。

【0014】圧縮ロールを用いる圧縮成形法について以下に説明する。圧縮ロールを用いる圧縮成形機は、ロール式造粒機として市販されている。ロール式造粒機として工本3．7kWの二本のロール式（径160mmφ、幅60mm）成形機を用いた場合の運転条件は、例えば、以下のとおりである。尚、ロールには平滑、溝付き、波付き等がある。まず、上部ホッパに入れた粉体原料は、フィードスクリュー（0．75W）の回転により加圧されながらプレスローラ間に押し込まれる。ロール回転（15RPM）につれて、輸込まれた粉体は圧縮され、粒子が密になり、板状に形成される。食い込み点から下のロールの間隙の減少割合が成形圧を決め、成形体の比重及び強度を決定する。圧力は油圧シリンダーにより目的の圧力に調整する。

【0015】本発明法により2種の沈殿法シリカを混合造粒することによって分散性が良く、しかも加工性、生産性、ゴム補強性の良好なシリカ造粒体が得られる。本発明法のシリカ造粒体及びその製造方法に用いられる沈殿法シリカは望ましくは、BET比表面積が150～250m²／g、吸油量が150～250ml／100gのものが良い。本発明法の造粒体をエラストマーに充填する方法は公知の方法が特に制限されず採用できる。例えば、SBR等有機固形ゴムへの混練においてはロールあるいはバンバリーミキサー等を用いて行うことができる。

【0016】

【実施例】以下、本発明の実施例を説明する。尚、各実施例の粒子硬度、分散性、加工性、エラストマー組成物の物性試験及び未加硫物の物性試験（ムーニー粘度試験）の測定は以下に示す方法で行った。

1）粒子硬度測定法

カーボンブラック粒子硬度測定法のJIS K6221．6．3．3造粒粒子の硬さ測定法に準じて測定した。

2）嵩比重

一定重量をメスシリンダーに流し込み、その時の数値を読み取り重量で割った数値とした。

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【0017】3）生産性
造粒時の生産性が高いものを○、普通のものを△、悪いものを×で表示した。
4）分散性
加硫ゴム片の目視判定及び加硫物性について、優れているものを◎、普通のものを○で表示した。
5）加工性
嵩比重が高く1バッチに仕込める量が多い程、ロール混練作業時の作業性、投入性は優れており、優れているものを○、中間のものを△、悪いものを×で表示した。
6）加硫物特性（引張強度）
ＪＩＳ　Ｋ６３０１の試験法に準じ測定した。
7）ムーニー粘度
ムーニー粘度計（島津製作所製，ＳＭＶ－２００型粘度計）を用い、温度１２５℃でＬ型ローターにて測定した。
【0018】実施例1～3及び比較例1
平均粒度１８５μｍｍ，嵩比重２５０ｇ／リットル，ＢＥＴ比表面積２００ｍ²／ｇ，粒子硬度１９ｇ．吸油量２００ｍｌ／１００ｇの沈殿シリカ（商品名；ニップシール（Ｎｉｐｓｉｌ）ＡＱ）１００部に対してニップシールＡＱを粉砕して平均粒度約１８μｍｍ，嵩比重１２５ｇ／リットルの沈殿シリカ（沈殿シリカＡ）５．２０．３０又は４０部をロール加圧式造粒機（ターボ工業社製，テスト機ＷＰ２３０－８０）を用いて，ロール間隙2．１ｍｍ．圧縮圧０．５トン／ｃｍ，及びロール回転数１５．６ｒｐｍで混合造粒し，さらに粒度を１ｍｍ～５ｍｍの範囲に調整し．表１に示す嵩比重２７６～３００ｇ／ｌ，粒子硬度１９～２２ｇの沈殿シリカ造粒体を得た。尚，粉体のフィードは６０ｍｍφのスクリューフィダーを用いて１６０ｒｐｍで実施した。このときの粉体供給速度は約１３０～１５０ｋｇ／ｈｒであった。
【0019】次いで，上記で得た造粒体５０部とスチレン・ブタジエン共重合体ゴム（ＳＢＲ１５０２；日本合成ゴム社製）１００部，加硫活剤として亜鉛２．０部，加硫促進剤として市販のＤ（ジフェニルグアニジン）１．２部，ＤＭ（ジベンゾチアジルジスルフィド）０．８部及び加硫助剤として，酸化亜鉛３部とステアリン酸１部，更に活性剤としてＰＥＧ（ポリエチレングリコール）＃４０００（第一工業薬品製）２部を８インチロールを用いて練り温度３０℃にて混練し，ゴム組成物を得た（実施例１～３，比較例１）。上記４点のゴム組成物について未加硫のもの及び加硫物（１５０℃で１０分間加硫したもの）について各種物性試験を行い，ロール混練時の加工性評価と合わせて結果を表２に示した。

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【0020】実施例4～6
平均粒度８５μｍｍ，嵩比重２２０ｇ／リットル．ＢＥＴ比表面積１９０ｍ²／ｇ，粒子硬度１６ｇ．吸油量２１０ｍｌ／１００ｇの沈殿シリカ（商品名；ニップシール（Ｎｉｐｓｉｌ）ＡＱ－Ｓ）１００部に対してニップシールＡＱ－Ｓを粉砕して平均粒度約１８μｍ．嵩比重１２７ｇ／リットルの沈殿シリカ（沈殿シリカＢ）５，２０又は３０部をロール加圧式造粒機を用いて実施例１～３と同様に混合造粒し，さらに粒度を１ｍｍ～５ｍｍの範囲に調整し，表１に示す嵩比重２８５～２９０ｇ／ｌ．粒子硬度２０～２１ｇの沈殿シリカ造粒体を得た。得られた造粒体を実施例１～３と同様の組成で混練し，ゴム組成物を得た（実施例４～６）。これらのゴム組成物について未加硫のもの及び加硫物（１５０℃で１０分間加硫したもの）について各種物性試験を行い，ロール混練時の加工性評価と合わせて結果を表２に示した。
【0021】比較例2～4
実施例１～３で２種混合造粒に用いた沈殿シリカの内，ニップシールＡＱを単独で実施例１～３と同様の条件でロール加圧式造粒機で造粒後，粒度を調整した（比較例２）。実施例１～３で２種混合造粒に用いた沈殿シリカの内，沈殿シリカＡを単独で実施例１～３と同様の条件でロール加圧式造粒機で造粒後，粒度を調整した（比較例３）。ニップシールＡＱを微粉砕し平均粒径１０μｍｍ．嵩比重８０ｇ／リットルの微粉末とし，造粒しないものを沈殿シリカＣとして得た（比較例４）。これらのシリカを用いて，実施例１～３と同様にしてゴム組成物を得，各ゴム組成物について未加硫のもの及び加硫物（１５０℃で１０分間加硫したもの）について各種物性試験を行い，ロール混練時の加工性評価と合わせて結果を表２に示した。
【0022】
【表１】

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例 / 配合	実施例						比較例			
	1	2	3	4	5	6	1	2	3	4
Nipsil AQ	100	100	100	–	–	–	100	100	–	–
Nipsil AQ-S	–	–	–	100	100	100	–	–	–	–
沈殿シリカA	5	20	30	–	–	–	30	–	100	–
沈殿シリカB	–	–	–	5	20	30	–	–	–	–
沈殿シリカC	–	–	–	–	–	–	–	–	–	100
粒子強度 (g)	22	19	21	20	21	20	20	22	19	–
嵩比重 (g/l)	234	300	234	280	288	285	278	275	282	80
生産性	○	○	○	○	○	△	△	△	×	×

【0023】 ＊ ＊【表2】

	実施例						比較例			
	1	2	3	4	5	6	1	2	3	4
スチレンーブタジエンゴム	100	100	100	100	100	100	100	100	100	100
沈降シリカ配合量 (phr)	50	50	50	50	50	50	50	50	50	50
加工性	○	○	○	○	○	○	△	△	×	×
分散性	○	○	○	○	○	○	○	○	○	●
ムーニー粘度 ML_{1+4}	111	113	109	108	110	105	112	112	110	114
引張強度 (kg/cm²)	271	272	275	276	273	278	268	278	272	280

【0024】表1及び2から明らかなように，本実施例の造粒品は，分散性，加工性，引張強さが，比較例4の沈降シリカCと，ほぼ同等の値を示した。このことは，本発明の造粒シリカは，嵩比重が大きくなったにも拘わらず，ゴム組成物中に均一に分散配合されていることを示す。又，造粒品を得る際の生産性については，造粒前の沈降シリカの嵩比重が極端に小さくなることもなく，更には造粒機でのワンパスの収率も優れており，トータルでの生産性も優れていることが分かる。

【0025】

【発明の効果】本発明によれば，エラストマー補強充填剤として必要な分散性及び補強性が良好であり，一定以上の粒子径を有し，かつ粒子強度が高い沈降シリカ造粒体，及びその製造方法を提供することができる。さらに本発明によれば，上記のように優れた物性を有するエラストマー補強用充填剤を得ることができる。